

Amendments to the Specification

Please insert the following new paragraphs (also incorporated originally into the specification by reference) after the paragraph ending at page 17, line 20:

The following instructive text is quoted from WO 85/03510, which document also is incorporated above in its entirety for all purposes.

“The hydrophobe associative copolymer is preferably an addition copolymer of a water-soluble ethylenically unsaturated monomer and an amphiphilic ethylenically unsaturated monomer having sufficient concentration of hydrophobic groups to enable the copolymer to associate with the hydrophobic groups of other molecules of the copolymer and sufficient concentration of nonionic, hydrophilic groups to enable the copolymer to control its hydro-philic-lyophilic balance. Thus, in the absence of electrolyte, the nonionic, hydrophilic groups of the amphiphilic monomeric portion of the copolymer are hydrated when the copolymer is dispersed in an aqueous medium. However, when electrolyte is then added to the aqueous medium, the hydrophilic groups of the amphiphilic monomer dehydrate and become hydrophobic.

Exemplary preferred polymers include copolymers of from 90 to 99.995, more preferably from 98 to 99.9, most preferably from 99 to 99.5, mole percent of one or more water-soluble monomers with from 0.005 to 10, more preferably from 0.1 to 2, most preferably from 0.5 to 1, mole percent of one or more amphiphilic monomers. For these copolymers, it is found that preferred amounts of amphiphilic monomer will vary with the molecular weight of the-copolymer. For example, a hydrophobe associative copolymer having a weight average molecular weight near 200,000, preferably contains from 1 to 2 mole percent of the amphiphilic monomer. Alternatively, the copolymer having a weight average molecular weight of 2 million preferably contains from 0.02 to 0.1 mole percent of amphiphilic monomer, preferably from 0.05 to 0.1 mole percent. Also, the preferred percentage of amphiphilic monomer varies with the relative balance of hydrophilic moiety versus the hydrophobic moiety in the amphiphilic monomer. For

example, as the balance shifts from hydrophilic to hydrophobic generally less amphiphilic monomer is employed. Conversely, if this balance shifts to more hydrophilic, then more of the amphiphilic monomer is required.

Suitable water-soluble monomers include those which are sufficiently water-soluble to form at least a 10 weight percent solution when dissolved in water and readily undergo addition polymerization to form polymers which are water-soluble. Exemplary water-soluble monomers include ethylenically unsaturated amides such as acrylamide, methacrylamide and fumaramide and their N-substituted derivatives such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS), N-(dimethylaminomethyl)acrylamide as well as N-(trimethylammoniummethyl) acrylamide chloride and N-(trimethylammoniumpropyl) methacrylamide chloride; ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid and fumaric acid; and other ethylenically unsaturated quaternary ammonium compounds such as vinylbenzyl trimethyl ammonium chloride, sulfoalkyl esters of unsaturated carboxylic acids such as 2-sulfoethyl methacrylate, aminoalkyl esters of unsaturated carboxylic acids such as 2-aminoethyl methacrylate, vinyl amines such as vinyl pyridine and vinyl morpholine, diallyl amines and diallyl ammonium compounds such as diallyl dimethyl ammonium chloride, vinyl heterocyclic amides such as vinyl pyrrolidone, vinylaryl sulfonates such as vinylbenzyl sulfonate as well as the salts of the foregoing monomers. Of the foregoing water-soluble monomers, acrylamide and combinations of acrylamide and acrylic acid, including salts of acrylic acid such as sodium acrylate or ammonium acrylate, are preferred. Acrylamide and combinations thereof with up to 75 mole percent of acrylic acid or salt thereof, based on total water-soluble monomer, are more preferred. Most preferred are polymers wherein the water-soluble monomer is a mixture of acrylamide with from 5 to 50 mole percent, especially from 5 to 30 mole percent of acrylic acid or salt thereof.

Suitable amphiphilic monomers include those which are (1) usually soluble in water at room temperature, but are water-insoluble at the temperature used to copolymerize the amphiphilic monomer with water-soluble monomer, e.g., about 60°C, and (2) ethylenically unsaturated compounds having hydrophobic groups and hydrophilic

groups as defined hereinbefore. Preferred amphiphilic monomers include the higher alkyl (polyoxyethylene)_x esters of α,β -ethylenically unsaturated carboxylic acids wherein x is a number from 2 to 40, most preferably from 5 to 40, and the higher alkyl has from 6 to 20 carbons, most preferably from 8 to 16. Examples of such esters include dodecyl poly(oxyethylene)₁₀ methacrylate, dodecyl poly(oxyethylene)₂₀ methacrylate, dodecyl poly(oxyethylene)₁₂ acrylate, tridecyl poly(oxyethylene)₁₄ methacrylate, tetradecyl poly(oxyethylene)₁₆ acrylate, bis(octa-decyl poly(oxyethylene)₁₂] itaconate, bis[hexadecyl poly(oxyethylene)₁₇] maleate, and other higher alkyl poly(oxyethylene) esters of acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and aconitic acid. Suitable amphiphilic monomers include alkylaryl poly(oxyethylene)_x esters of the aforementioned unsaturated acids, especially those wherein alkyl has from 7 to 10 carbons and x is as defined before. Examples of such alkylaryl esters include nonyl- α -phenyl poly(oxyethylene)₁₀ acrylate, nonyl- α -phenyl poly(oxyethylene)₁₂ methacrylate, dodecyl- α -phenyl poly(oxyethylene)₂₀ methacrylate, and the like. Other suitable amphiphilic monomers include higher alkyl, copoly(oxyethylene/oxypropylene) esters of the aforementioned acids, N-(higher alkyl poly(oxyethylene)) acrylamides and methacrylamides, N-(higher alkyl copoly(oxyethylene/oxypropylene)) acrylamides and methacrylamides and the like. Of the preferred higher alkyl poly(oxyethylene)_x esters, most preferred are those wherein alkyl. has from 8 to 16 carbons, x is from 5 to 40, and the acid portion is acrylate or methacrylate, e.g., dodecyl poly(oxyethylene)₁₀ methacrylate, dodecyl poly(oxyethylene)₂₀ methacrylate, and similar acrylate esters. In applications wherein hydrolysis is a problem such as in caustic floods, N-(higher alkyl copoly(oxyethylene/oxypropylene) acrylamides are the most preferred amphiphilic monomers.

The aforementioned hydrophobe associative copolymers are advantageously prepared by copolymerizing the water-soluble monomers with amphiphilic monomers in an aqueous medium containing a chelating agent that complexes with any existing polymerization inhibitors and an emulsifier that solubilizes the amphiphilic monomer in the aqueous medium. The polymerization techniques are typically those wherein the amphiphilic monomer or mixture of amphiphilic monomers is added with vigorous

agitation to an aqueous solution of the water-soluble monomer or mixture of water-soluble monomers and solubilizing emulsifier. By solubilizing the amphiphilic monomer in the aqueous medium, it is meant the combination of aqueous medium, amphiphilic monomer and emulsifier gives the visual appearance of a-clear solution, preferably, the "solvated" particles of monomer are less than 200 Angstrom units. A chelating agent such as ethylenediamine tetraacetic acid (EDTA), the pentasodium salt of (carboxymethylimino)bis(ethylenenitrilo)tetraacetic acid, tetrasodium ethylenedinitrilotetraacetate or the trisodium salt of N-(carboxymethyl)-N'-(2-hydroxyethyl)-N,N'-ethylenediglycine is then added to the reaction mixture to complex metallic salts which are often present in water-soluble monomers such as acrylamide. The copolymerization is then preferably initiated by adding a polymerization initiator capable of generating free -radicals. Optionally, a chain transfer agent may be included in the polymerization reaction mixture.

The solubilizing emulsifier is required in most instances to suitably solubilize the amphiphilic monomer and to subsequently obtain a hydrophobe associative copolymer having a desirable concentration of hydrophobic moieties in the copolymer. It is believed that the amphiphilic monomer is solubilized in the micelles formed by the emulsifier. Thus, the emulsifier is generally employed in an amount which is above the critical micelle concentration (CMC) of the emulsifier, but less than that which reduces the concentration of amphiphilic monomer in the copolymer to a point that the hydrophobic groups of the copolymer will not associate in the presence of the electrolyte. Preferably, the concentration of emulsifier in the aqueous polymerization medium is from 2 to 4 times the CMC of the emulsifier. The amount of emulsifier used will also be such that there is at least one amphiphilic monomer molecule per micelle of the emulsifier, preferably from 1 to 10, most preferably from 2 to 5, amphiphilic monomer molecules per micelle. For example, when sodium dodecyl sulfate (NaDS) is employed as an emulsifier for dodecyl poly(oxyethylene)₁₀ methacrylate (DPMA), the molar ratio of DPMA to NaDS is at least 1:50 and up to 1:2, preferably from 1:5 to 1:25, most preferably from 1:10 to 1:15. By knowing the CMC, the hydrophilic-lipophilic balances (HLB) and aggregation number of molecules in the micelle molecular weight of an

emulsifier and the hydrophobicity of the amphiphilic monomer, suitable molar ratios and appropriate emulsifier concentrations can be determined for any given amphiphilic monomer and emulsifier to provide similar suitable concentrations of hydrophobic moieties in the hydrophobe associative copolymer. In general mole ratios which will provide from 2 to 10, preferably from 4 to 5, molecules of the amphiphilic monomer per micelle of emulsifier are selected.

Suitable emulsifiers include anionic agents such as alkali metal salts of alkyl sulfates and alkyl and aryl sulfates, e.g., dodecyl alkyl sulfosuccinates and sodium dodecylbenzene sulfate; fatty acid soaps, e.g., sodium oleate, sodium stearate and potassium oleate; alkali metal salts of sulfonated fatty alcohols, e.g., sodium dodecyl sulfate; sulfates of ethoxylated alcohols; alkyl phosphate esters, e.g., dodecyl hydrogen phosphate; fluoro emulsifiers, e.g., perfluoroalkyl sulfates; and the like. Also included are cationic emulsifiers such as alkylamine hydrochlorides, e.g., dodecylamine hydrochloride and tridecylamine hydrochloride; quaternary alkyl or aryl ammonium halides such as dodecyl trimethyl ammonium chloride; ethoxylated fatty amines and other emulsifiers as described in McCutcheon's Detergents and Emulsifiers, North American Edition, 1980 Annual. In general, when the hydrophilic/hydrophobic polymer is anionic or nonionic, an anionic emulsifier such as an alkali metal alkyl sulfate is preferably employed as the emulsifier. When the hydrophobe associative copolymer is cationic, a cationic emulsifier such as dodecylamine hydrochloride is employed. When the hydrophobe associative copolymer is nonionic, anionic or cationic, a nonionic emulsifier such as nonylphenoxy polyethylene glycol having 10 ethyleneoxy units per molecule or other water-30 -dispersible nonionic surfactants as defined herein is suitably employed.

Suitable chelating agents include those mentioned hereinbefore, with the pentasodium salt of (carboxymethylimino)bis(ethylenenitrilo)tetraacetic acid being preferred. When employed, the chelating agent is used in an amount in the range from 0.1 to 0.2, preferably from 0.1 to 0.15, weight percent based on the weight of total monomers.

Exemplary suitable polymerization initiators include the inorganic persulfates such as potassium persulfate, ammonium persulfate and sodium persulfate, azo catalysts such as azobisisobutyronitrile and dimethyl azoisobutyrate; organic peroxygen compounds such as benzyl peroxide, t-butyl peroxide, diisopropyl benzene hydroperoxide and t-butyl hydroperoxide. Of these initiators, the oil-soluble types such as the organic peroxides and azo compounds are preferred. It is desirable to employ from 0.01 to 0.1 weight percent of initiator based on the weight of total monomers.

The hydrophobe associative copolymers are readily recovered from the aqueous medium when such is desired by removal of water under vacuum or by azeotropic distillation or by drum drying. Alternatively, the aqueous medium containing the hydrophobe associative copolymer can be used as such.

It is also understood that hydrophobe associative copolymers of acrylamide, acrylic acid and amphiphilic monomer can be prepared by copolymerizing all three of these monomers or by copolymerizing acrylamide with the amphiphilic monomer and subsequently hydrolyzing a portion of the copolymerized acrylamide by contacting the copolymer with a base such as sodium hydroxide and/or sodium carbonate."

Please correct the paragraph beginning on page 17, line 21 as follows:

Compositions disclosed here, as already discussed above, comprise water soluble hydrophobe associative polymer and alkali metal salt of carboxylic acid. In accordance with one aspect, the hydrophobe associative polymer has functionality including at least sulfonate groups, carboxylate groups and hydrophobes associative with one another in a saturated aqueous solution of an alkali metal salt of a carboxylic acid. In accordance with another aspect, the hydrophobe associative polymer is a polymerization reaction product of reactants comprising AMPS reactant, alpha, beta-unsaturated carbonyl reactant and hydrophobe reactant as discussed above. It will be apparent to those skilled in the art that quantities of other ingredients suitable to the intended use

may be present in the composition. For example, compositions intended for use in or as a well drilling or other well servicing fluid may also contain, salts such as sulfates, nitrates and bicarbonates, and other ingredients. Such salts [will] inevitably will be present where sea water or other naturally occurring brine is used in preparing the compositions. If desired, the hydrophobe associative polymer composition may also contain an antioxidant, e.g. [2-mercaptopbenothiazole] 2-mercaptobenzothiazole and/or other suitable additives. When [2-mercaptopbenothiazole] 2-mercaptobenzothiazole is used, it may be incorporated in the same proportion, w/v, as the water soluble polymer.

In the paragraph beginning on page 22, line 17, please make the following amendments:

Example I

In this Example I a hydrophobe associative polymer in accordance with the above disclosure is synthesized. All amounts are in grams.

1.	Acrylic acid	68.45g
2.	Lauryl methacrylate	0.64
3.	0.1% Methylenebisacrylamide	3.37
4.	Deionized water	99.58
5.	[Acrylamidopropanesulfonate]	49.22
5.	<u>Acrylamidopropanesulfonate</u>	<u>49.22</u>
6.	29% Ammonia	69.61
7.	1% Sodium bromate	0.50
8.	1% Sodium persulfate	5.00
9.	1% Sodium metabisulfite	1.50

Ingredients 1, 2, 3 and 4 were weighted into a 600 ml beaker. The beaker was placed in a water bath set at 5 degrees C with stirring. Ingredient 5 was then added and dissolved. When ingredient 5 was completely dissolved, ingredient 6 was added, keeping the temperature less than 30 degrees C. After ingredient 6 was completely added, the bath temperature was set to 30 degrees C. The beaker is sparged with nitrogen and after 60 minutes initiator ingredients 7 and 8 were added. The vessel was stirred for 5 minutes after which ingredient 9 was added and then stirred for one minute. Stirring and nitrogen sparge were stopped and the beaker was removed from the water bath and set in an insulated container where the temperature increased to about 100 degrees C in 30 to 60 minutes. The polymer reaction product was dried to less than 10% moisture and then ground to a powder.

--THE REMAINDER OF THIS PAGE INTENTIONALLY LEFT BLANK--